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(54) **An inkjet recording paper and a manufacturing process thereof.**

(57) An ink jet recording paper comprises a base paper wherein at least one surface has a recording layer. This recording layer contains at least 40 weight % of a pigment and no more than 60 weight % of a binder, the surface roughness by ten point height on the recording layer surface being no more than 5 μm, and the air permeability of the recording paper being no more than 1,000 seconds. In a process for manufacturing the paper, a surface of the base paper coated with a recording layer solution is dried in contact with a heated mirror finishing surface.

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This invention relates to an ink jet recording paper for recording with a water-based ink, and in particular to an ink jet recording paper which provides high recording quality.

In ink jet recording, small ink drops are released by a variety of different mechanisms so as to form a dot image on printing paper. Unlike the case of dot impact printing, this method is not noisy, makes it easy to obtain full color images, and permits printing to be performed at high speeds.

However, as the ink used in ink jet recording is usually a water-based ink based on a direct dye or acidic dye, it has poor drying properties.

The properties required of the paper used in ink jet recording are as follows:

(1) Permits fast ink drying,

(2) Permits high printing speeds,

(3) Gives little spreading, tailing or blurring of dots.

Conventionally, property (1) was improved by providing an ink jet recording layer comprising a silica of large specific surface area so as to increase ink absorption. However, if the ink absorption is increased too much, the print density falls. A method was therefore developed to control the amount of voids in recording paper in order to solve this problem, as is described in Japanese Tokko Sho 63-22997.

Due to recent progress in ink jet printers and more diverse needs, a requirement has emerged for better resolution and higher image quality. However, using an ink jet recording paper having a recording layer with a pigment of large specific surface area, the recording layer surface has low smoothness. As a result, the appearance of the image was lacking in quality, the dots were not perfect circles, and the reproducibility of the image was unsatisfactory.

To improve the smoothness of the recording layer surface, conventional pigment-coated ink jet recording papers were given a supercalendar treatment or other treatment. This improved gloss and smoothness, but the porous structure of the ink jet recording layer was destroyed. Consequently, ink absorption amount and ink absorption speed declined, and drying properties were poorer.

There are also resin-coated ink jet recording papers which have a relatively smooth surface. However, as this type of paper contains almost no pigments of large specific surface area, ink absorption amount and absorption speed were low.

In ink jet recording, aqueous ink where a dye is dissolved in water are used, but if the water adheres to the paper, the image tends to blur and run after printing. In the case of resin-coated papers, water-soluble resins are generally used, so this tendency was particularly marked.

After carrying out many studies on ink jet recording papers to solve the aforesaid problems, the Inventors found it was possible to obtain a recording surface of high gloss and smoothness, obtain a large ink absorption amount and high ink absorption speed, and confer water resistance on the image. These discoveries led to the present invention.

It is therefore an object of this invention to provide an ink jet recording paper which has a recording layer of high surface smoothness, gives an image of very high quality appearance, and permits large ink absorption amount and speed.

The aforesaid objects of this invention are attained by an ink jet recording paper characterized in that it comprises a base paper wherein at least one surface has a recording layer, this recording layer containing at least 40 weight % of a pigment and no more than 60 weight % of a binder, the surface roughness by ten point height on the recording layer surface being no more than 5 μm, and the air permeability of the printing paper being no more than 1,000 seconds.

As described hereinafter, the pigment used in this invention may be selected from any of those used for ink jet recording papers known in the art, but it is preferable that its specific surface area is 40 - 600 m^2/g.

Although coated layers containing such pigments generally have good ink absorption, their surface gloss is poor. The gloss and smoothness are improved by giving the paper a supercalendar treatment or other treatment, but as this breaks down the porous structure of the paper, ink absorption declines.

According to this invention, to achieve the dual objectives of ink absorption and smoothness, a drying method is used wherein the wet surface after coating is placed in pressure contact with a heated mirror finished surface. This drying method is the same as the cast coated paper manufacturing method defined in JISP0001 (6043).

If this method is used, the mirror finished surface is transferred without breaking down the porous structure of the coated surface, so both high ink absorption and smoothness can be attained. However, using this drying method, the air permeability is not always less than 1,000 seconds regardless of the composition of the coating solution, and in the case of for example an ordinary cast coated paper for printing, it is of the order of 1,500 seconds. Pigment-coated printing papers with an air permeability of more than 1,000 seconds have a low ink absorption and absorption speed, and consequently cannot be used for ink jet recording.

According to this invention, with a recording layer containing a pigment of specific surface area 40 - 600

m^2/g and concurrent use of the aforesaid drying method, it has for the first time become possible to obtain an ink jet recording paper wherein the surface roughness by ten point height on the recording layer surface is no more than 5 μm, and the air permeability of the paper is no more than 1,000 seconds.

There is no particular limitation on the pigment used in the invention provided that its specific surface area is 40 - 600 m^2/g. This pigment may be chosen from any of those known in the art, for example silica, white carbon or silica gel prepared by the wet method, or superfine silica prepared by the dry method, or a material such as a calcium carbonate silica complex having a particle structure consisting of silica crystallized in calcium carbonate crystals, may also be used. Mixtures of these pigments may also be used. In particular, if a calcium carbonate silica complex is used, a recording layer having an excellent gloss can be obtained.

According to this invention, the blending proportion of pigment in the recording layer is preferably 40 weight % or more, but more preferably lies in the range 45 weight % to 80 weight %.

There is no particular limitation on the binder used in the invention provided that it is an aqueous binder. This binder may be chosen from resins known in the art such as casein, starch, polyvinyl alcohol, carboxymethyl-cellulose, styrenebutadiene latex and vinyl acetate emulsions, these resins being used either alone or in admixture. In particular, if the gelation cast coating method, which is a coagulation method, is used, the resin used is preferably casein. The blending proportion of the binder in the recording layer is preferably no more than 60 weight %, but more preferably lies in the range 20 weight % to 55 weight %.

According to this invention, it is preferable to use a cationic polymer electrolyte concurrently with the aforesaid binding agent. This electrolyte reacts with anionic groups such as sulfonic acid in the water-soluble direct dye or water-soluble acidic dye molecule so as to form salts which are insoluble in water, thereby improving the water resistance of the recorded image.

Examples of such cationic polymer electrolytes are polyvinylbenzyltrimethylammonium halide, polydiacryldimethylammonium halide, polydimethylaminoethylmethacrylate hydrochloride, polyethyleneimine, dicyandiamideformalin condensate, epichlorhydrin modified polyalkylamine, polyvinylpyridium halide, quaternary ammonium salts and polyamines. The blending proportion of the cationic polymer electrolyte is preferably 1 - 30 weight %, but more preferably 5 - 20 weight %, of the total weight of binder.

The ink jet recording layer according to this invention may if necessary, in addition to the aforesaid pigments and binders, also contain various additives such as dispersants, antifoaming agents, dyes or fluidity modifying agents.

The ink jet recording layer according to this invention may be applied by any suitable coating method known in the art using a coating tool such as a blade coater, air knife coater, curtain coater, bar coater, gravure coater or comma coater.

The coating weight is 2 - 50 g/m^2 but preferably 6 - 30 g/m^2 in terms of solids on each surface, this amount being adjusted as desired so as to cover the surface of the base paper and obtain sufficient ink absorption.

The ink jet recording layer according to this invention is dried, as described hereintofore, by bringing the wet coated surface into pressure contact with a heated mirror finished surface. There are the following three kinds of the coated layer state; ① the state obtained immediately after coating before the coating has dried, ② the state obtained by gelating the coating before it has dried, ③ the plasticized state obtained by re-wetting the coating after drying it.

According to this invention, of the aforesaid states, it is preferable to use the gelated state. Typical coagulating agents used in the coagulation method are for example the calcium, zinc, barium, lead, magnesium, cadmium or aluminum salts of formic acid, acetic acid, citric acid, tartaric acid, lactic acid, hydrochloric acid or sulfuric acid, or potassium sulfate, borax or boric acid. The salts of formic acid are most preferable in this invention.

The heated mirror finished surface used in this invention generally refers to a drum having a mirror-polished cylindrical outer surface heated to about 100°C.

Examples of the base paper used in this invention are ordinary wood-free or medchanical papers.

The recording paper of this invention may be used for ordinary offset printing or the like, or it may be used as PPC paper.

As described hereintofore, by selecting the composition of the coated layer and drying method, the ink jet recording paper of this invention gives not only gloss but also improved smoothness of the recording surface, provides high ink absorption and ink absorption speed, and confers water resistance on the image. Further, as the surface has high smoothness, the image has a high quality appearance, and as the dots produced are almost perfectly round, the image has excellent reproducibility.

EXAMPLES

This invention will now be described in more detail by means of specific examples, but it will be understood

that it is not to be construed as being limited by these examples in any way.

Example 1

A 30% concentration coating solution comprising, in terms of solid composition, 60 weight % of a calcium carbonate silica complex of specific surface area 60 m^2/g (Finesil CM-F: Tokuyama Soda co. Ltd.) as pigment; 35 weight % of casein (lactic casein from New Zealand); 4 weight % of the quaternary ammonium salt of polyethyleneimine as binder; and 1 weight % of calcium stearate (Nopcoat C-104: San nopco Co. Ltd.) as releasing agent, was applied by a roll coater to a wood-free paper of weighting 90 g/m^2 and air permeability 45 seconds. The coating was then congulated by applying a 10 weight % aqueous solution of calcium formate.

Next, while the coated layer was still wet, it was brought into pressure contact with the mirror surface of a casting drum heated to 90 °C so as to dry it, thereby obtaining an ink jet recording paper according to this invention. The coating weight in this case was 19.0 g/m^2 in terms of dry weight. The following tests were performed on the ink jet recording paper obtained, and the results are shown in Table 1.

(1) Surface roughness by ten point height
Measured according to JIS B0601.

(2) Air permeability
Measured by an Oken type Air Permeability Tester according to J. TAPPI No. 5B

(3) Gross at 75 degree
Measured according to JIS 28741.

(4) Dot density
After printing with a color ink jet printer (IO-725: Sharp Co. Ltd.), the reflection density was measured using a Konica Microdensitometer PDM-5 (Konica Co. Ltd.), and expressed as an average value for 5 dots.

(5) Roundness coefficient
The dot circumference and area were measured using an image analyzer (ADS Co.Ltd), and the value obtained by the following equation was taken as the roundness coefficient:

$$\text{Roundness coefficient} = \frac{1}{\frac{(\text{Circumference})^2}{\text{Area}} \times \frac{1}{4\pi}}$$

Example 2

A 30% concentration coating solution comprising, in terms of solid composition, 40 weight % of a synthetic silica of specific surface area 600 m^2/g (Syloid 600: Fuji Davison co. Ltd.) as pigment; 15 weight % of styrene butadiene latex (JSR-0801: Japan Synthetic Rubber co Ltd.) ; 20 weight % of polyvinyl-alcohol (PVA-117: Kuraray co. Ltd.); 20 weight % of casein; 4 weight % of the quaternary ammonium salt of polyethyleneimine as binder; and 1 weight % of calcium stearate as releasing agent, was applied by a roller to a wood-free paper of weighting 90 g/m^2 and air permeability 45 seconds, as in Example 1. The coating was then coagulated by applying a 10 weight % aqueous solution of calcium formate. Next, while the coated layer obtained was still wet, it was brought into pressure contact with the mirror surface of a casting drum heated to 90°C so as to dry it, thereby obtaining an ink jet recording paper according to this invention wherein the coating weight was 16.0 g/m^2 in terms of dry weights. The results of tests performed on the ink jet recording paper thus obtained are shown in Table 1.

Example 3

A 30% concentration coating solution comprising, in terms of solid composition, 60 weight % of a calcium carbonate silica complex of specific surface area 80 m^2/g (Finesil CM-F) as pigment; 15 weight % of styrene butadiene latex (JSR-0801: Japan Synthetic Rubber co.Ltd.) ; 20 weight % of casein (lactic casein from New Zealand); 4 weight % of the polydimethylaminoethylmethacrylate chloride as binder; and 1 weight % of calcium stearate as releasing agent, was applied by a roller coater to a wood-free paper of weighting 90 g/m^2 and air permeability 45 seconds as described in Example 1. Next, the coating was coagulated by applying a 10 weight % aqueous solution of calcium formate and brought into pressure contact with the mirror surface of a casting drum heated to 90°C so as to dry it, thereby obtaining an ink jet recording paper according to this invention wherein the coating weight was 14.0 g/m^2 in terms of dry weights. The results of tests performed on the ink jet recording paper thus obtained are shown in Table 1.

Comparative Example 1

A recording paper was obtained by exactly the same procedure as in Example 1, excepting that a synthetic silica of specific surface area 30 m^2/g (Finesil SP-20: Tokuyama Soda co.Ltd.) was used instead of the calcium carbonate silica complex (Finesil CM-F) used as pigment in Example 1. The coating weight of the recording paper obtained was 18.0 g/m^2 in terms of dry weights. The test results are shown in Table 1.

Comparative Example 2

A recording paper was obtained by exactly the same procedure as in Example 2, excepting that a synthetic silica of specific surface area 700 m^2/g (FK700: Degusa Ltd.) was used instead of the synthetic silica (Syloid 600) used as pigment in Example 2. The coating weight of the recording paper obtained was 16.0 g/m^2 in terms of dry weights. The test results are shown in Table 1.

Comparative Example 3

A 30% concentration coating solution having exactly the same solid composition as that of Example 1, was applied by a roller coater to a paper of weighting 90 g/m^2. The coating was air-dried in the normal way without coagulation, and then given a supercalendar treatment so as to obtain a recording paper. The coating weight of the recording paper obtained was 18.5 g/m^2 in terms of dry weight. The test results are shown in Table 1.

Comparative Example 4

A recording paper was obtained by exactly the same procedure as in Example 1, excepting that a coating layer was obtained having a solid composition of 5 weight % of the silica of specific surface area 60 m^2/g (Finesil CM-F) used as pigment in Example 1, 90 weight % of casein, 4 weight % of the quartenary ammonium salt of poly-ethyleneimine as binder and 1 weight % of calcium stearate as releasing agent. The coating amount of the recording paper obtained was 19.0 g/m^2 in terms of dry weights. The test results are shown in Table 1.

Comparative Example 5

A test was performed using a commercial cast coated paper of weighting 93 g/m^2 (Espricoat F: Nippon Paper Industries co. Ltd.). The test results are shown in Table 1.

Table 1

	Pigment type	Pigment specific surface area (m^2/g)	Pigment blending proportion in coating layer (wt %)	Drying method	Coating weight (g/m^2)	surface roughness by ten point height (μm)	Air permeability (sec)	gloss at 75 degree (%)	Ink absorption	Dot density	Roundness coefficient
Example 1	Calc. carb. silica complex	60	60	Mirror surface pressure contact	19.0	1.0	750	86.3	○	0.88	0.83
Example 2	Synthetic silica	600	40	Mirror surface pressure contact	16.0	3.5	650	78.5	○	0.76	0.79
Example 3	Calc. carb. silica complex	80	40	Mirror surface pressure contact	16.0	1.9	710	88.2	○	0.83	0.75
Comparative Example 1	Synthetic silica	30	60	Mirror surface pressure contact	18.0	1.0	900	68.3	×	0.73	0.49
Comparative Example 2	Synthetic silica	700	40	Mirror surface pressure contact	16.0	3.3	530	83.3	○	0.63	0.71
Comparative Example 3	Calc. carb. silica complex	60	60	Air drying	18.5	9.5	250	5.5	○	0.81	0.40
Comparative Example 4	Calc. carb. silica complex	60	5	Mirror surface pressure contact	19.0	1.0	1300	90.5	×	0.93	0.79
Comparative Example 5	———	——	——	Mirror surface pressure contact	——	0.7	1500	89.7	×	0.38	Measurement impossible

In the table, calc. carb. refers to calcium carbonate

Claims

1. An ink jet recording paper characterized in that it comprises a base paper wherein at least one surface has a recording layer, this recording layer containing at least 40 weight % of a pigment and no more than 60 weight % of a binder, the surface roughness by ten point on the recording layer surface being no more than 5 μm, and the air permeability of the whole recording paper being no more than 1,000 seconds.

2. An ink jet recording paper as defined in Claim 1, wherein the specific surface area of the pigment lies in the range 40 - 600 m^2/g.

3. An ink jet recording papaer as defined in Claim 1 or 2, wherein the pigment is at least one pigment selected from a group comprising silica, white carbon or silica gel obtained by the wet method, superfine silica obtained by the dry method, and a calcium carbonate silica complex having a particle structure consisting essentially of silica crystallized in calcium carbonate crystals.

4. An ink jet recording paper as defined in Claim 3, wherein the main component of the pigment is a calcium carbonate silica complex having a particle structure consisting essentially of silica crystallized in calcium carbonate crystals.

5. An ink jet recording paper as defined in any one of Claims 1 - 3, wherein the blending proportion of the pigment lies in the range 45 weight % - 80 weight %.

6. An ink jet recording paper as defined in any one of Claims 1 - 5, wherein the binder is a water-soluble binder and/or an aqueous emulsion binder.

7. An ink jet recording paper as defined in Claim 6, wherein the binder is at least one binder selected from a group comprising casein, starch, polyvinyl alcohol, carboxymethylcellulose, styrene-butadiene latex and vinyl acetate emulsion.

8. An ink jet recording paper as defined in Claim 7, wherein the main component of the binder is casein.

9. An ink jet recording paper as defined in any one of Claims 1 - 8, wherein the recording layer further contains a cationic polymer electrolyte as part of the binder.

10. An ink jet recording paper as defined in any preceding Claim, wherein the gloss at 75 degree of the recording layer surface is at least 70%.

11. An ink jet recording paper as defined in any one of Claims 1 - 10, wherein the coating weight of the recording layer is 2 - 50 g/m^2.

12. A method of manufacturing an ink jet recording paper characterized in that a recording layer containing at least 40 weight % of a pigment and no more than 60 weight % of a binder is applied to one surface of a base paper, and the base paper surface coated with the recording layer coating solution is then brought while still wet into pressure contact with a heated mirror finishing surface so as to dry it.

13. A method of manufacturing an ink jet recording paper as defined in Claim 12, wherein the binder is coagulated while the coating is wet.

14. A method of manufacturing an ink jet recording paper as defined in Claim 13, wherein the coagulating agent which coagulates the binder is at leat one agent selected from a group comprising salts of formic acid, acetic acid, citric acid, tartaric acid, lactic acid, hydrochloric acid and sulfuric acid, potassium sulfate, borax and boric acid.

15. A method of manufacturing an ink jet recording paper as defined in Claim 14, wherein a salt of formic acid is used as the coagulating agent.

16. A method of manufacturing an ink jet recording paper as defined in Claim 15, wherein the main component of the binder is casein.

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EUROPEAN SEARCH REPORT

Application Number
EP 93 30 6149

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	US-A-4 778 711 (HIROYOSHI HOSOMURA ET AL) * claims 1-14 * ---	1,6,7,9, 11	B41M5/00
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			B41M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 November 1993	FOUQUIER, J

CATEGORY OF CITED DOCUMENTS

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